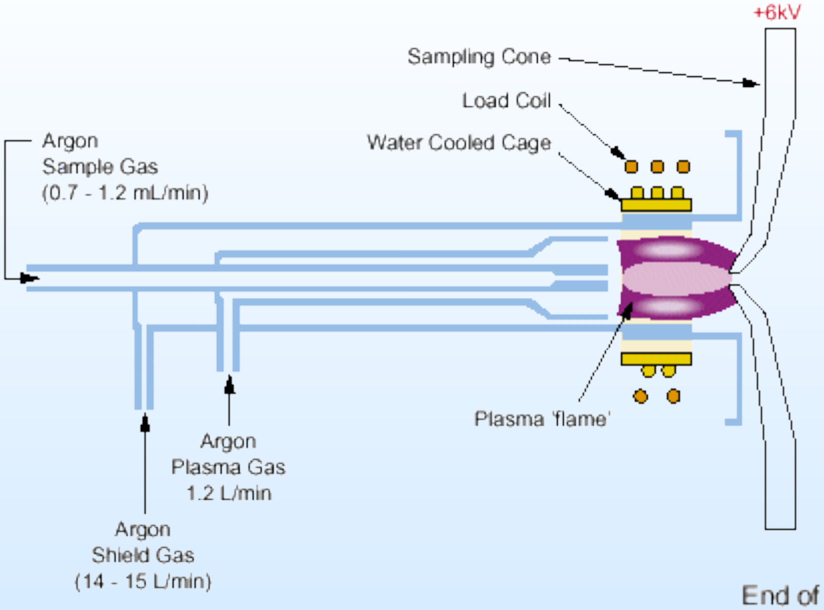
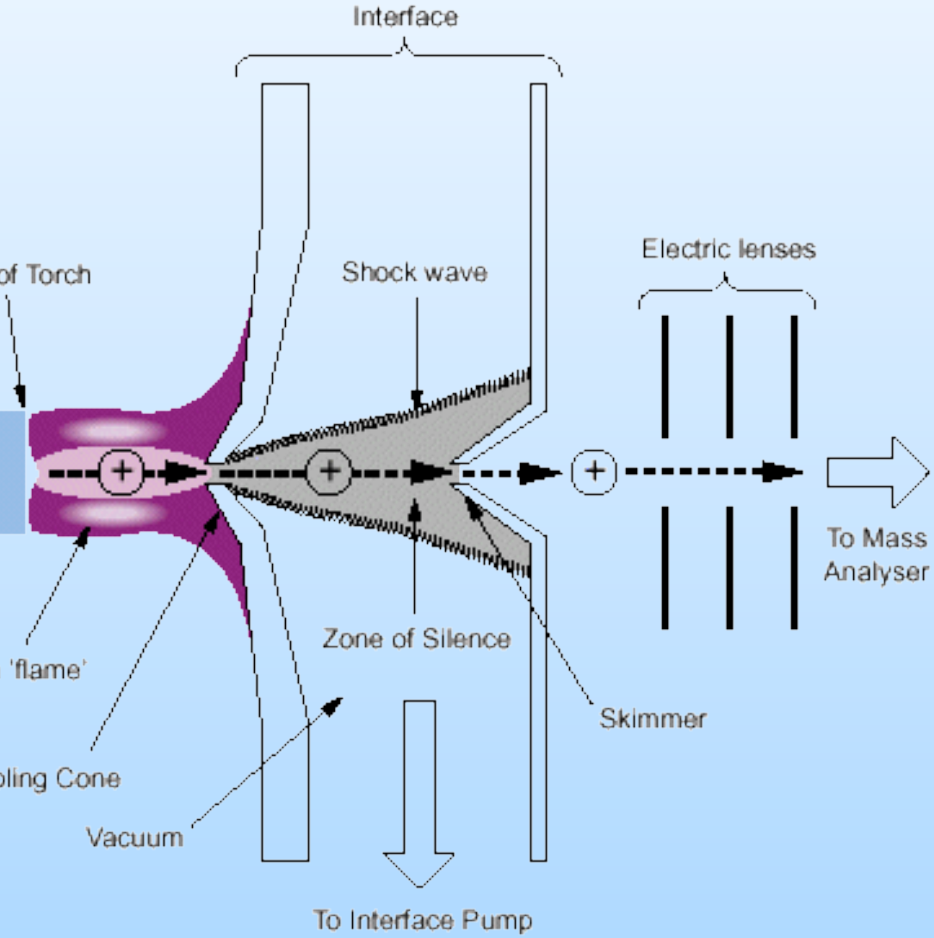
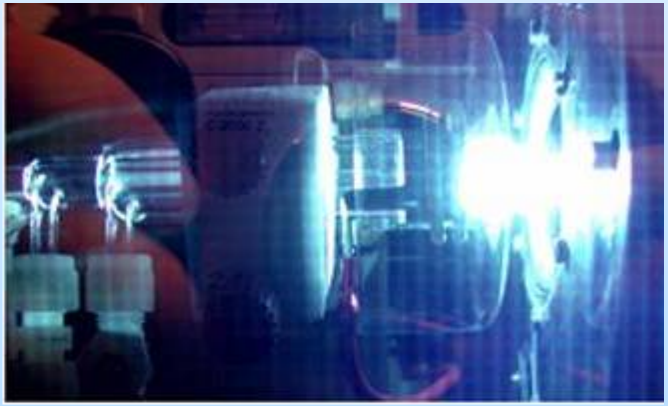


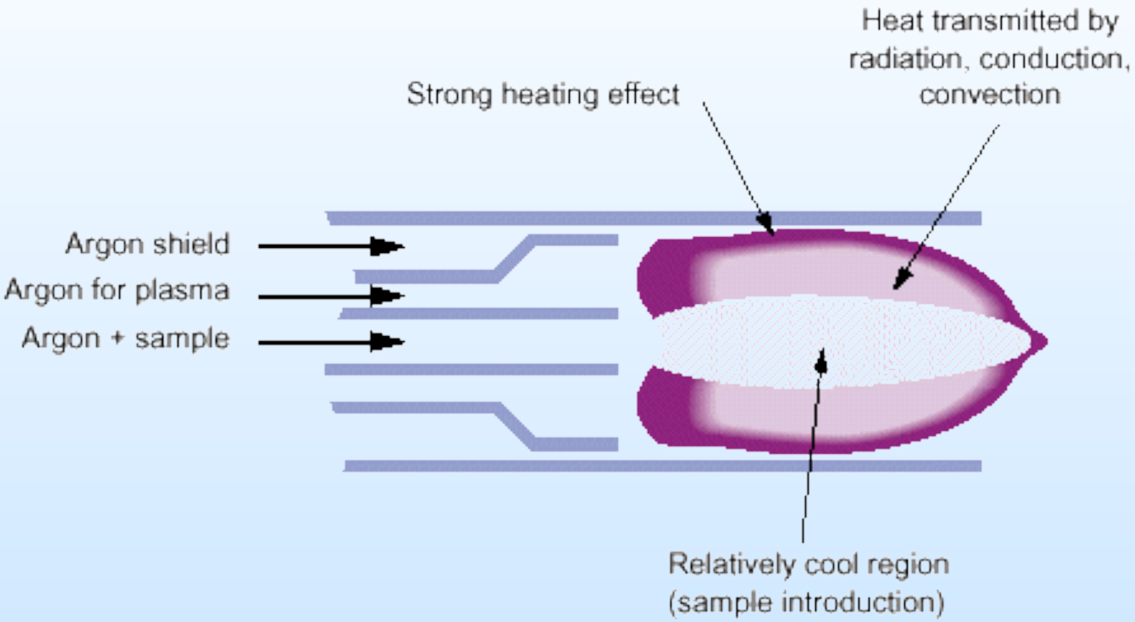
8,000 to 10,000 °C

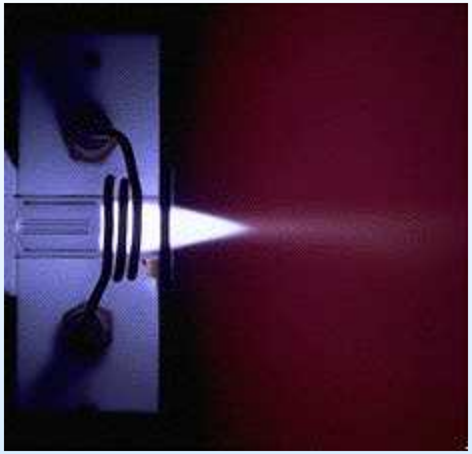




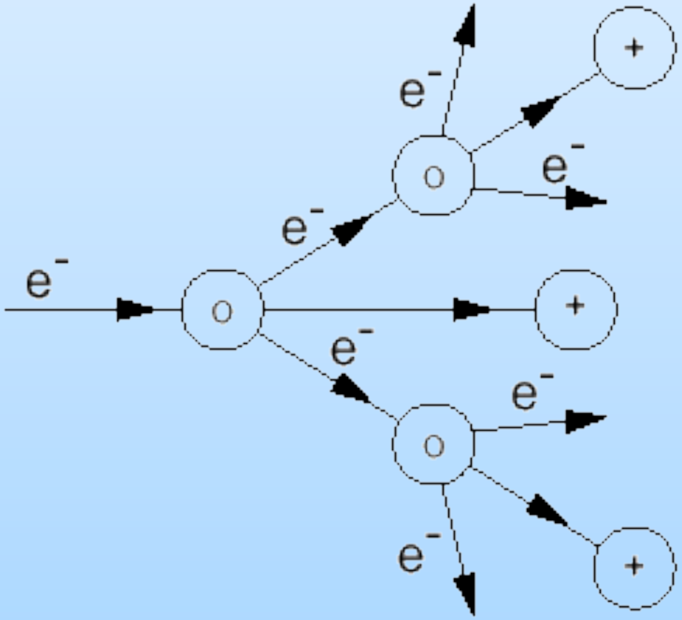
Plasma Torches

Plasma Torches





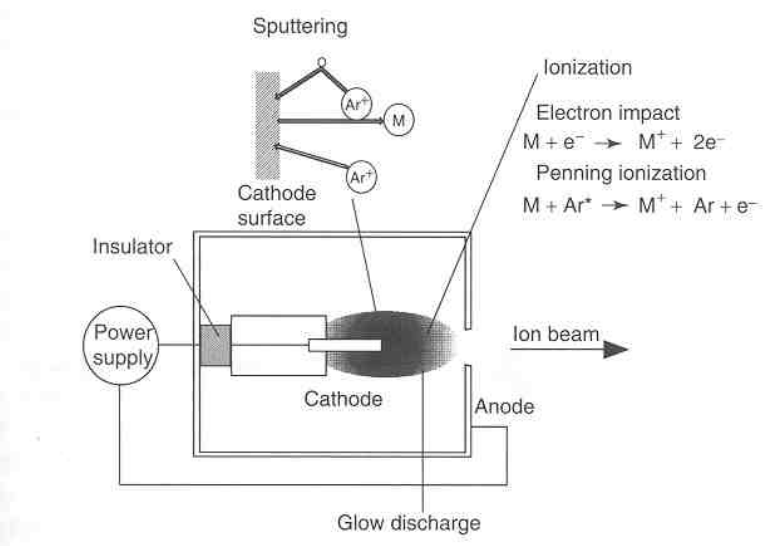
Gaseous phase containing neutral molecules, atoms, ions and electrons

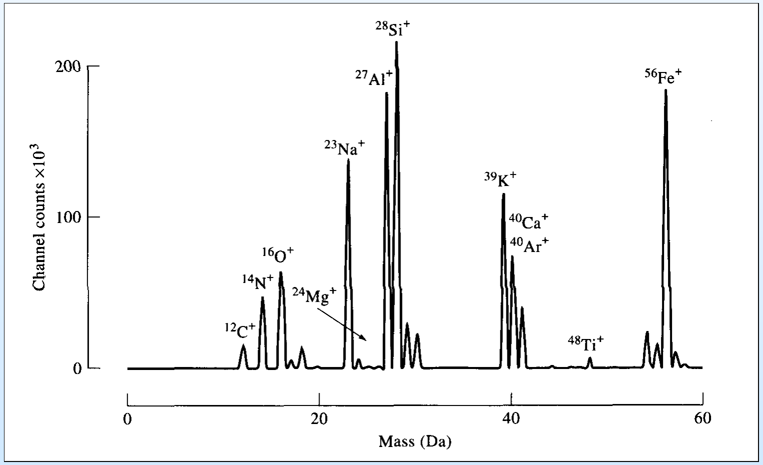


Ionization Mechanisms on a Plasma

$$\begin{array}{llll}
M + e^- & \longrightarrow & M^+ + 2e^- & \text{(a)} \\
 & & \quad \searrow F^+ + N^o & \\
N^o + e^- & \longrightarrow & N^+ + 2e^- & \text{(b)} \\
 & & \quad \searrow X^+ + Y^o & \\
M + e^- & \longrightarrow & M^* \longrightarrow A + B & \text{(c)} \\
A \text{ (or } B) + e^- & \longrightarrow & A^+ \text{ (or } B^+) & \text{(d)} \\
 & & \quad \searrow W^+ + Z^o & \\
M + Ar^+ & \longrightarrow & M^+ + Ar & \text{(e)} \\
M + Ar^* & \longrightarrow & M^+ + Ar & \text{(f)} \\
M + \overrightarrow{Ar} & \longrightarrow & \overrightarrow{M} + Ar & \text{(g)} \\
M + h\nu & \longrightarrow & M^* \longrightarrow A + B & \text{(h)} \\
\hdashline
Ar^+ + O_2 & \longrightarrow & ArO^+ + O & \text{(i)} \\
Ar^+ + O^1 & \longrightarrow & ArO^+ & \text{(j)} \\
\hdashline
ArO^+ + H_2 & \longrightarrow & Ar + H_2O^+ & \text{(k)}
\end{array}$$

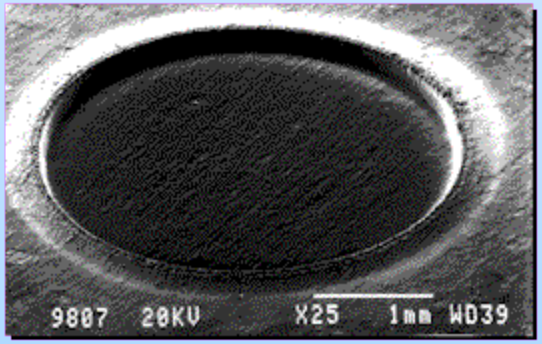
Inorganic Mass Spectrometry

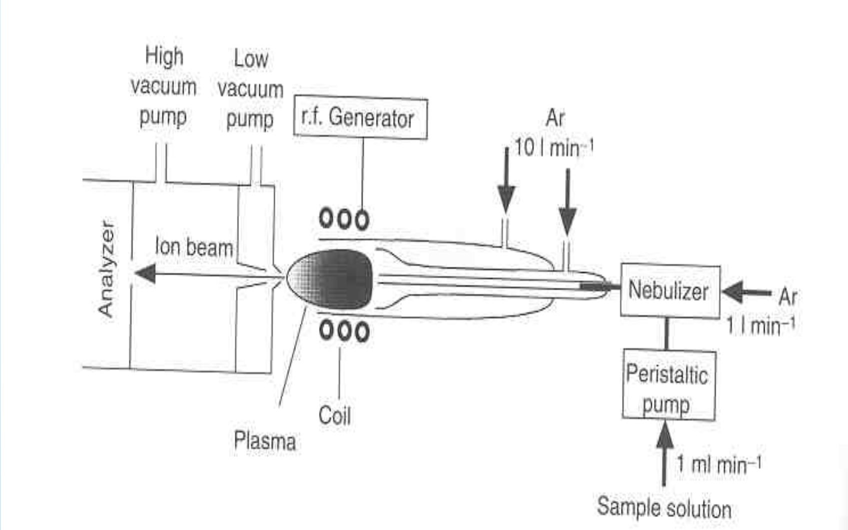




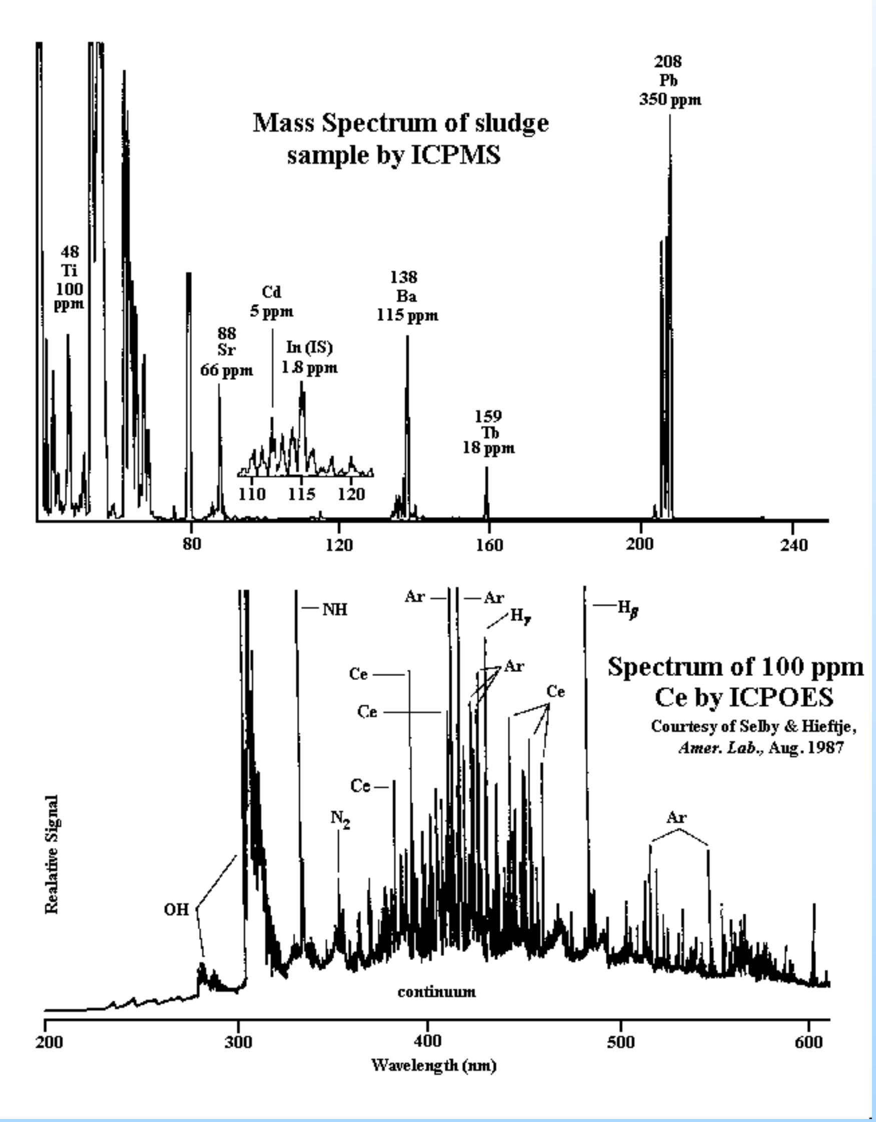
INDUCTIVELY COUPLED PLASMA

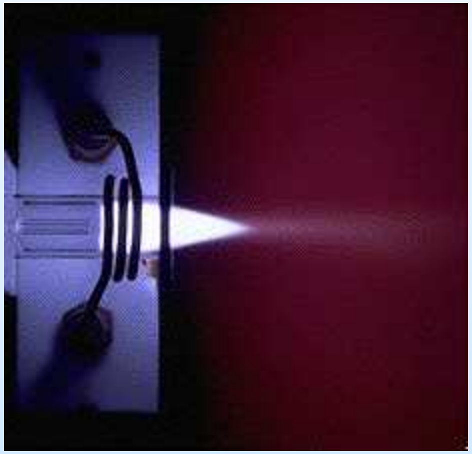
GLOW DISCHARGE



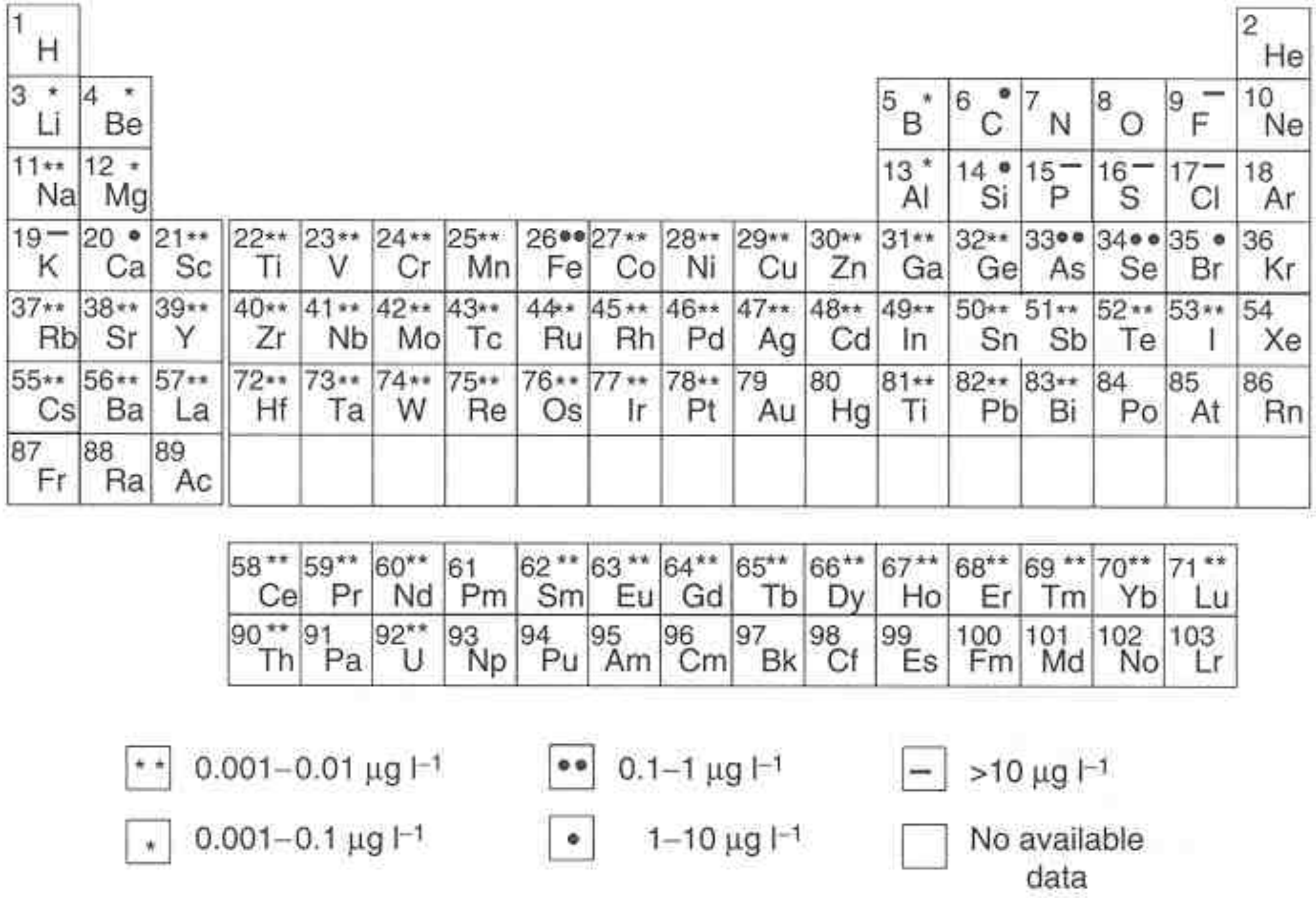


AES or MS?


Mass Spectrum of sludge sample by ICPMS
48
Ti
100
ppm
88
Sr
66 ppm
Cd
5 ppm
In (IS)
1.8 ppm
110
115
120
138
Ba
115 ppm
159
Tb
18 ppm
208
Pb
350 ppm
80
120
160
200
240
Spectrum of 100 ppm Ce by ICPOES
Courtesy of Selby & Hieftje, *Amer. Lab.*, Aug. 1987
NH
Ar
Ar
H_γ
H_β
Ce
Ce
Ar
Ce
Ce
N_2
OH
Ar
continuum
Realative Signal
200
300
400
500
600
Wavelength (nm)



Inorganic Mass Spectrometry



1 H																	2 He
3 * Li	4 * Be											5 * B	6 ● C	7 N	8 O	9 — F	10 Ne
11 ** Na	12 * Mg											13 * Al	14 ● Si	15 — P	16 — S	17 — Cl	18 Ar
19 — K	20 ● Ca	21 ** Sc	22 ** Ti	23 ** V	24 ** Cr	25 ** Mn	26 ●● Fe	27 ** Co	28 ** Ni	29 ** Cu	30 ** Zn	31 ** Ga	32 ** Ge	33 ●● As	34 ●● Se	35 ● Br	36 Kr
37 ** Rb	38 ** Sr	39 ** Y	40 ** Zr	41 ** Nb	42 ** Mo	43 ** Tc	44 ** Ru	45 ** Rh	46 ** Pd	47 ** Ag	48 ** Cd	49 ** In	50 ** Sn	51 ** Sb	52 ** Te	53 ** I	54 Xe
55 ** Cs	56 ** Ba	57 ** La	72 ** Hf	73 ** Ta	74 ** W	75 ** Re	76 ** Os	77 ** Ir	78 ** Pt	79 Au	80 Hg	81 ** Ti	82 ** Pb	83 ** Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

58 ** Ce	59 ** Pr	60 ** Nd	61 Pm	62 ** Sm	63 ** Eu	64 ** Gd	65 ** Tb	66 ** Dy	67 ** Ho	68 ** Er	69 ** Tm	70 ** Yb	71 ** Lu
90 ** Th	91 Pa	92 ** U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

** 0.001–0.01 μg l^{-1}

* 0.001–0.1 μg l^{-1}

●● 0.1–1 μg l^{-1}

● 1–10 μg l^{-1}

— >10 μg l^{-1}

☐ No available data

Figure 1.35
Analytical sensitivity of the elements by ICPMS

Isobaric Interferences and HRMS

Table 1. Example interferences and resolving power required.

Analyte	**Interference**	**Δm/M**	**R**
75As = 74.92160	40Ar35Cl = 74.93123	0.0096375	7788
52Cr = 52.94065	37Cl16O = 52.96081	0.0201653	2629
56Fe = 55.93494	40Ar16O = 55.95729	0.0223556	2505
40Ca = 39.96259	40Ar = 39.96238	0.00021 40	190476
87Sr = 86.9088987	Rb = 86.90918	0.00029 87	300000

Mass analyzers: why and how?

Once ions are generated they need to be "sorted" based on their masses

Three basic parameters

- Maximum mass range (1000, 2000, 225,000)
- Ion transmission (ion trapping)
- Resolution
- Pulsed vs. Continuous
- EQUATIONS OF MOTION!!!

Mass analyzers

Types of mass analyzers

MASS SPECTROMETERS

- **Magnetic**
- **Electrostatic**
- **Time of Flight**
- **Quadrupole Mass Filters**
- **Quadrupole Ion Traps**
- **Ion Cyclotron Resonance**

$$E_k = \frac{mv^2}{2} = qV = zV = zE$$

Ion accelerated through a potential field V

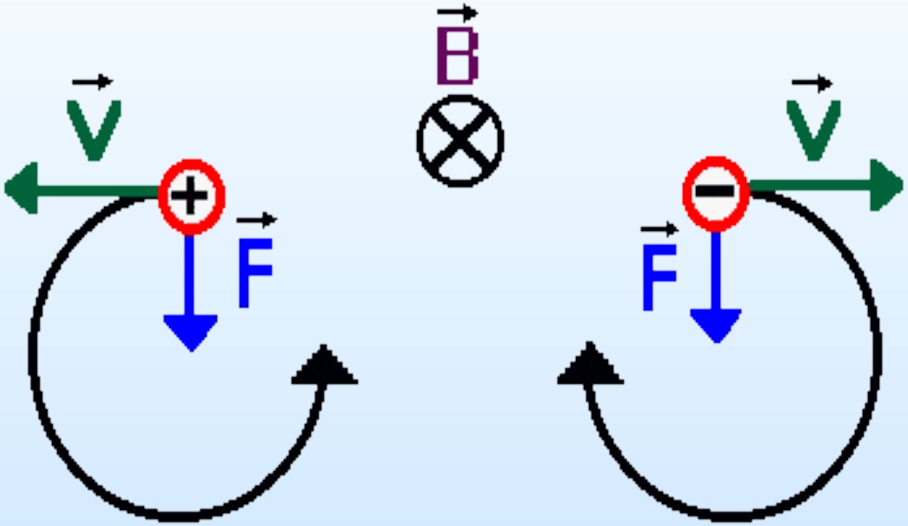
Mass Analyzers:

Analyzer	System Highlights
Quadrupole	Unit mass resolution, fast scan, low cost
Sector (Magnetic and/or Electrostatic)	High resolution, exact mass
Time-of-Flight (TOF)	Theoretically, no limitation for m/z maximum, high throughput
Ion Cyclotron Resonance (ICR)	Very high resolution, exact mass, perform ion chemistry

How do the analyzers work?

- Field instruments utilize the behavior of charged particles moving through field regions.
- Sector instruments incorporate an electromagnetic field and (usually) an electric field (for energy focusing).
- Quadrupole and ion trap instruments incorporate a combination of radio-frequency and direct-current fields. Ions entering a field experience a deflecting force, depending on the strength of the field and the mass-to-charge ratio of the ion.
- By scanning the field strength all the ions produced in the ion source are sequentially focused at the detector (which is usually a photomultiplier or an electron multiplier).

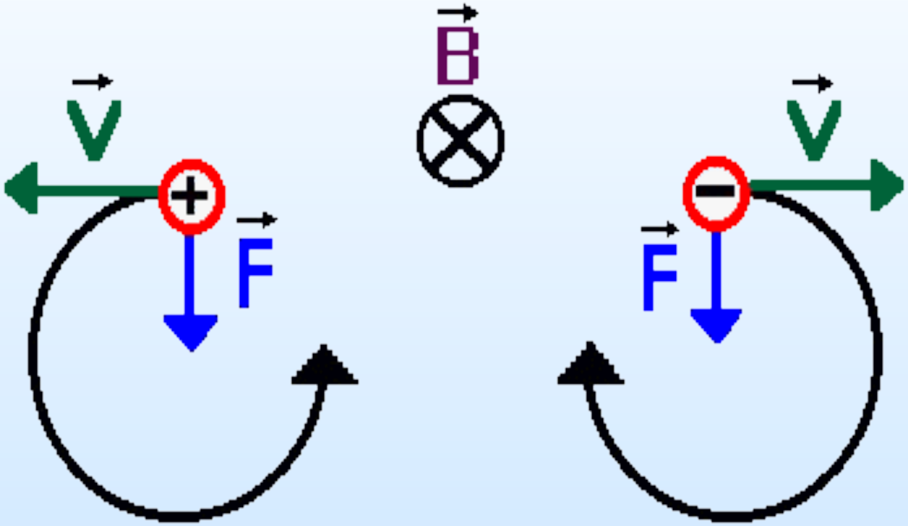
Magnetic field to separate ions?



$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}$$

Fleming’s Left-hand rule

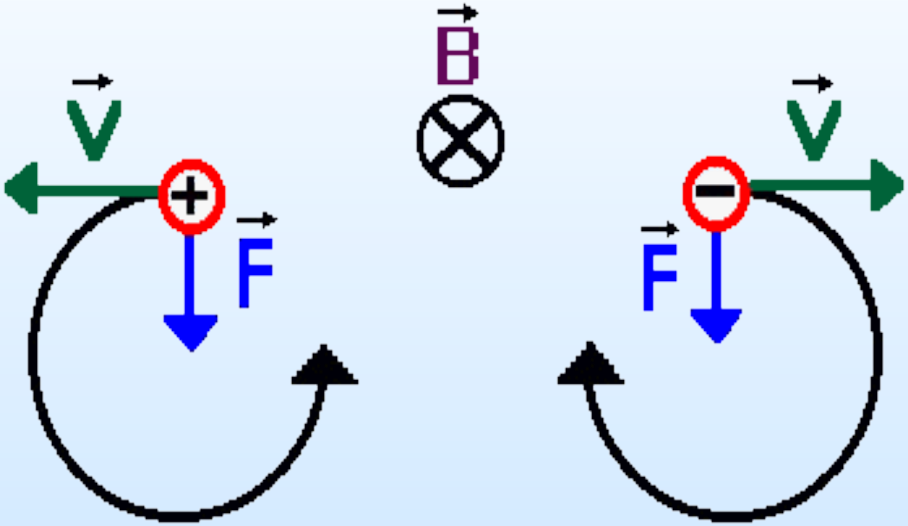
Magnetic field to separate ions?



$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}$$

$$\boxed{E_k = \frac{mv^2}{2} = qV} = zV = zE$$

Magnetic field to separate ions?



$$E_k = \frac{mv^2}{2} = qV_s$$

$$mv^2 = 2qV_s$$

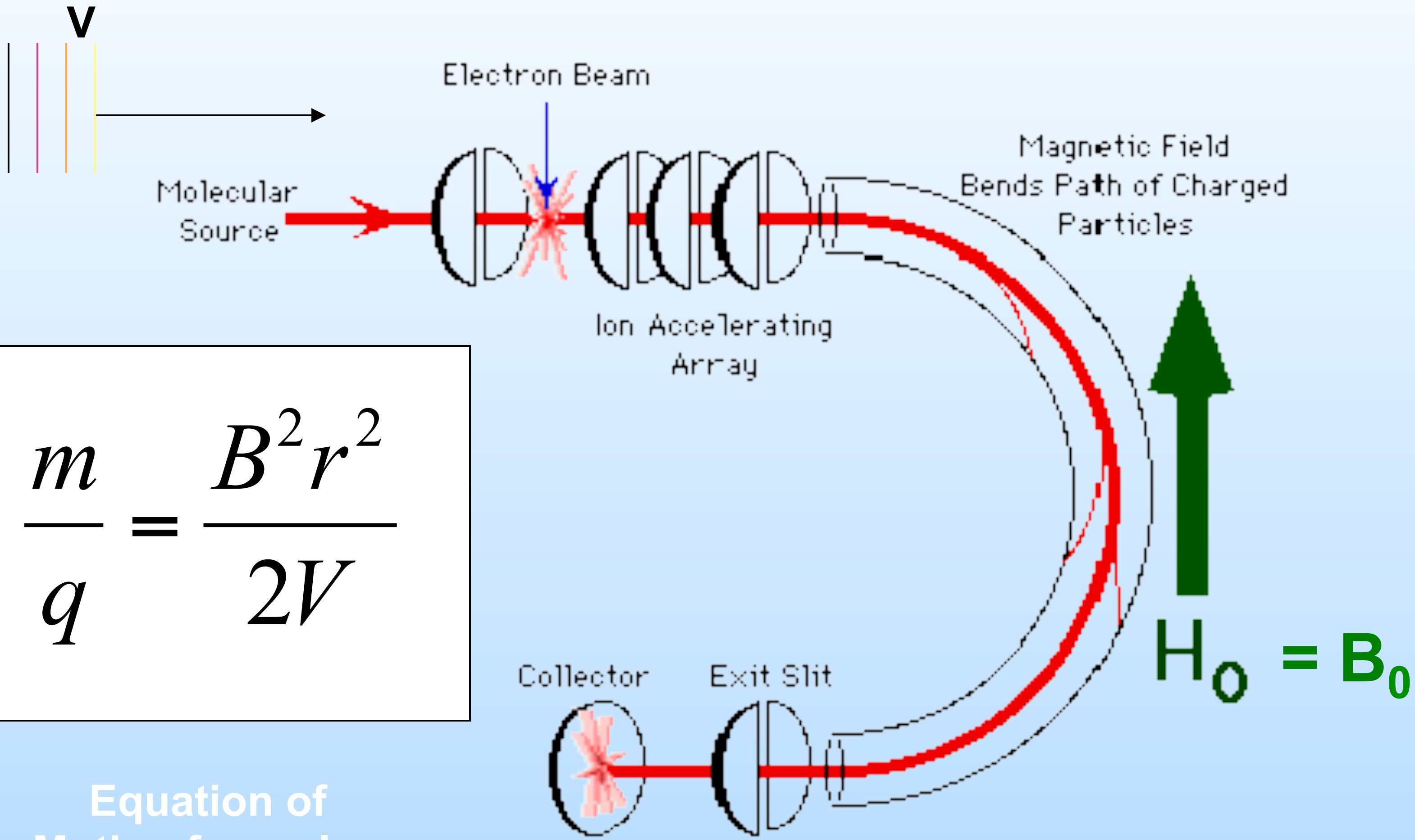
$$F_M = qvB$$

F_M = centrifugal force!

$$qvB = \frac{mv^2}{r} \text{ or } mv = qBr$$

$$r = \sqrt{\frac{2mV}{qB^2}}$$

Mass Analyzers: MAGNETIC SECTORS



$$\frac{m}{q} = \frac{B^2 r^2}{2V}$$

Equation of Motion for an Ion in a magnetic field

$$r = \sqrt{\frac{2mV}{qB^2}}$$

→m ∝ B^2 (constant V)
→m ∝ 1/V (constant B)
→m ∝ B^2/V

Ions in static or quasi-static electro-magnetic fields

Lorentz Force

$$\vec{F} = \underset{\text{Electric force}}{q\vec{E}} + \underset{\text{Magnetic force}}{q\vec{v} \times \vec{B}} \qquad \textbf{(1)}$$

q = electric charge

B = magnetic field

E = electric field

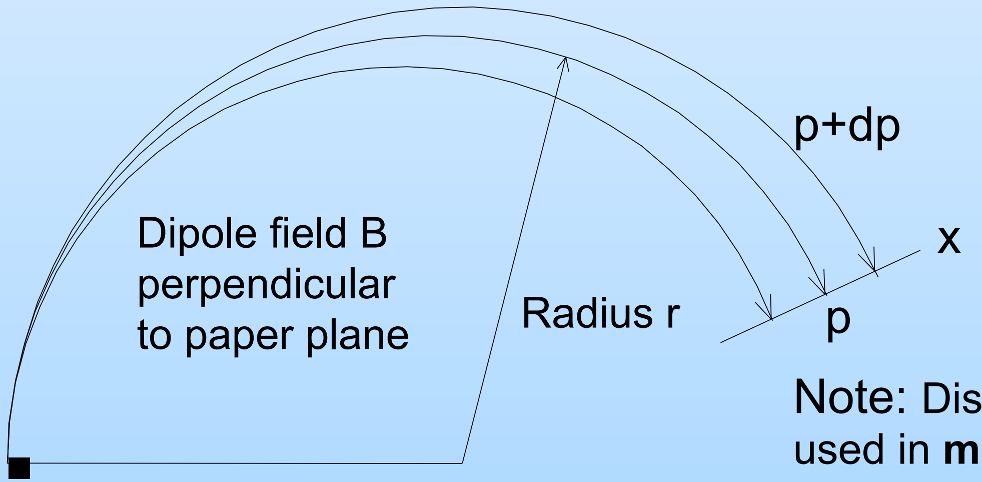
v = velocity

For ion **acceleration electric** forces are used.

For **momentum analysis** the magnetic force is preferred because the force is always perpendicular to **B**. Therefore v, p and E are constant.

Force in magnetic dipole B = const: $p = q\,B\,r$

p = mv = momentum
r = bending radius
Br = magn. rigidity

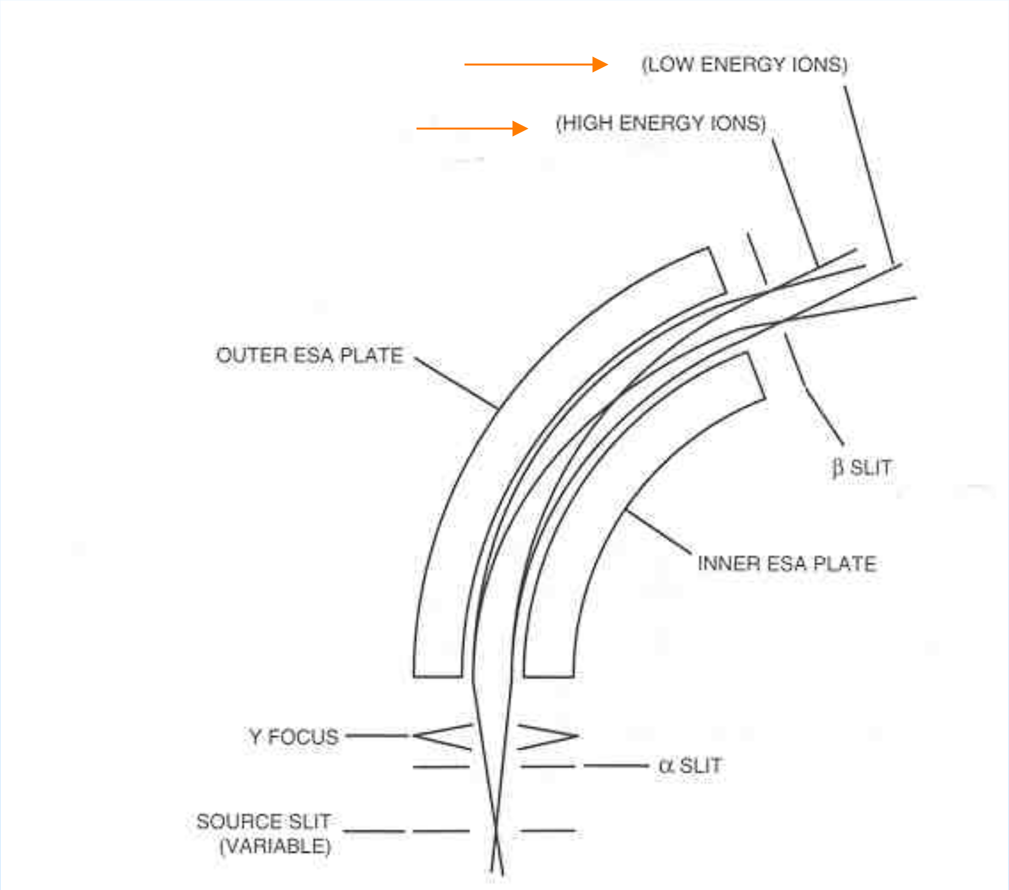


General rule:
Scaling of magnetic system in the linear region results in the **same ion-optics**

Note: Dispersion dx/dp used in **magnetic analysis**, e.g. Spectrometers, magn. Separators,

Electrical field to separate ions?

ESA = Electrostatic analyzer



$$E_k = \frac{mv^2}{2} = qV$$

$$qE = \frac{mv^2}{r}$$

$$\boxed{r} = \frac{2\boxed{E_k}}{qE}$$

ENERGY SEPARATOR!!!

Equation of Motion for an Ion in a electric “circular” field

Magnetic field to separate ions?

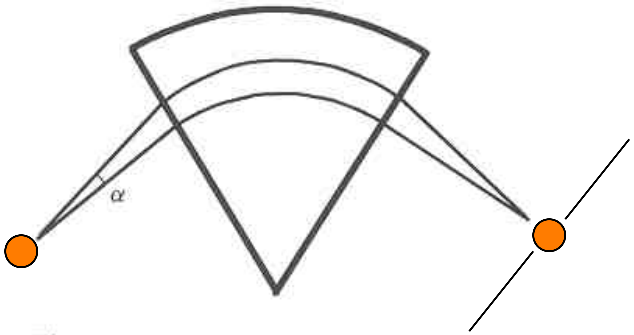


Figure 2.41
Direction focusing in a magnetic sector

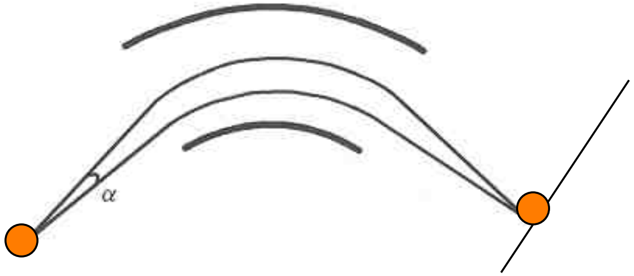
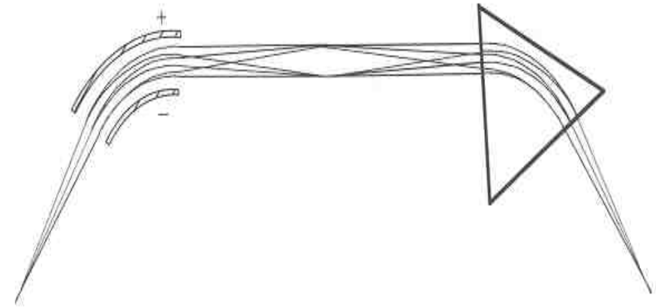


Figure 2.42
Direction focusing in an electric sector

If ions get into the sector at different angles they will converge at a focal point when they exit the sector



Magnetic field to separate ions?

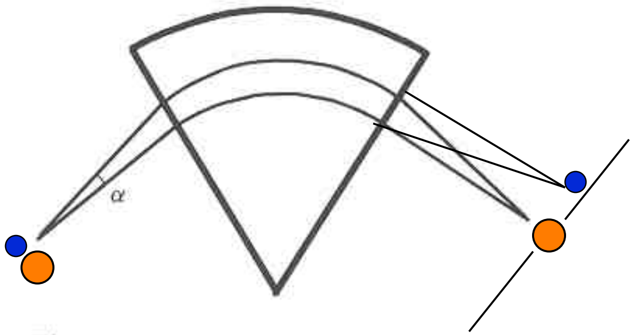


Figure 2.41
Direction focusing in a magnetic sector

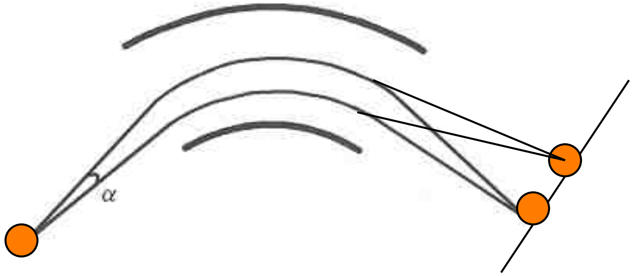
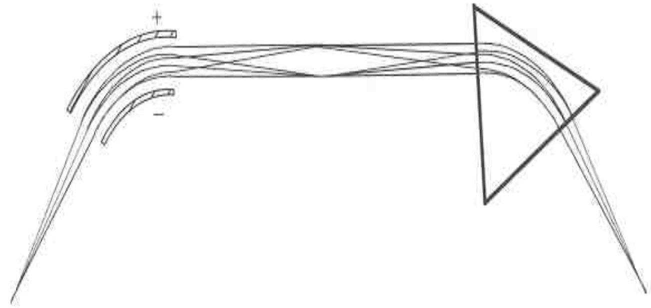


Figure 2.42
Direction focusing in an electric sector

If ions get into the sector at different angles they will converge at a focal point when they exit the sector



Mass Analyzers: MAGNETIC SECTORS

Benefits

- Classical mass spectra
- Very high reproducibility
- Best quantitative performance of all mass spectrometer analyzers
- High resolution
- High sensitivity
- High dynamic range
- Linked scan MS/MS does not require another analyzer
- High-energy CID MS/MS spectra are very reproducible

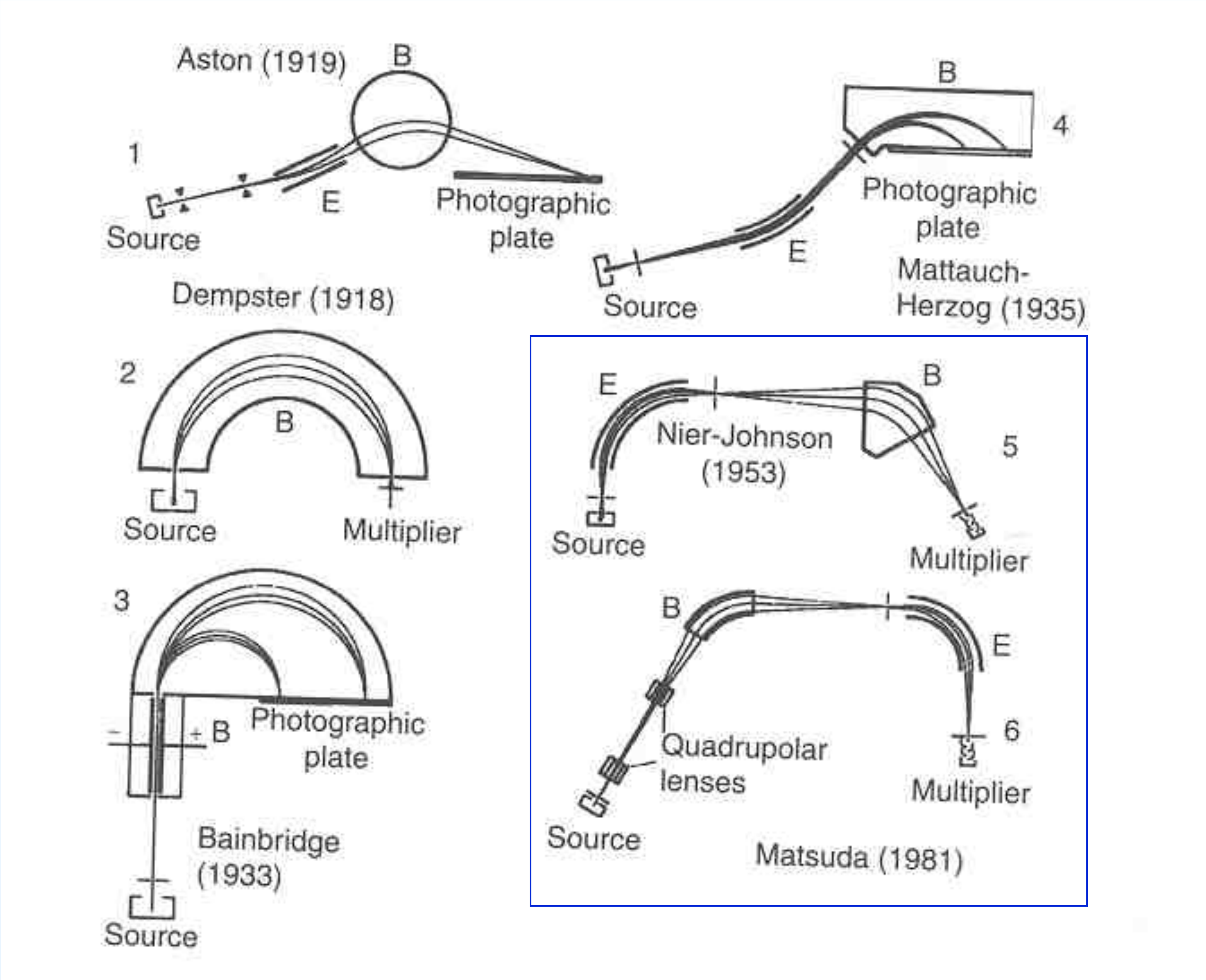
Limitations

- Not well-suited for pulsed ionization methods (e.g. MALDI)
- Usually larger and higher cost than other mass analyzers
- Linked scan MS/MS gives either limited precursor selectivity with unit product-ion resolution, or unit precursor selection with poor product-ion resolution

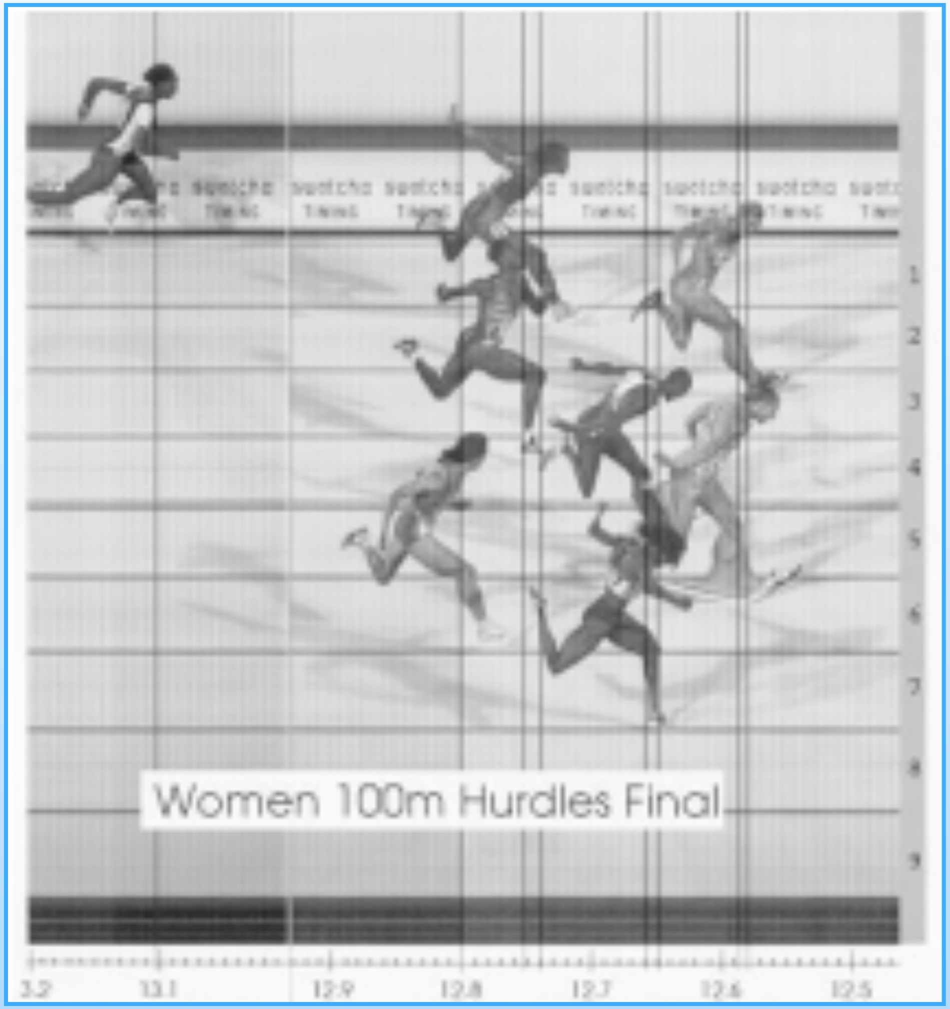
Applications

- All organic MS analysis methods
- Accurate mass measurements
- Quantitation
- Isotope ratio measurements

Sector geometries and double focusing



Time of Flight Analyzers

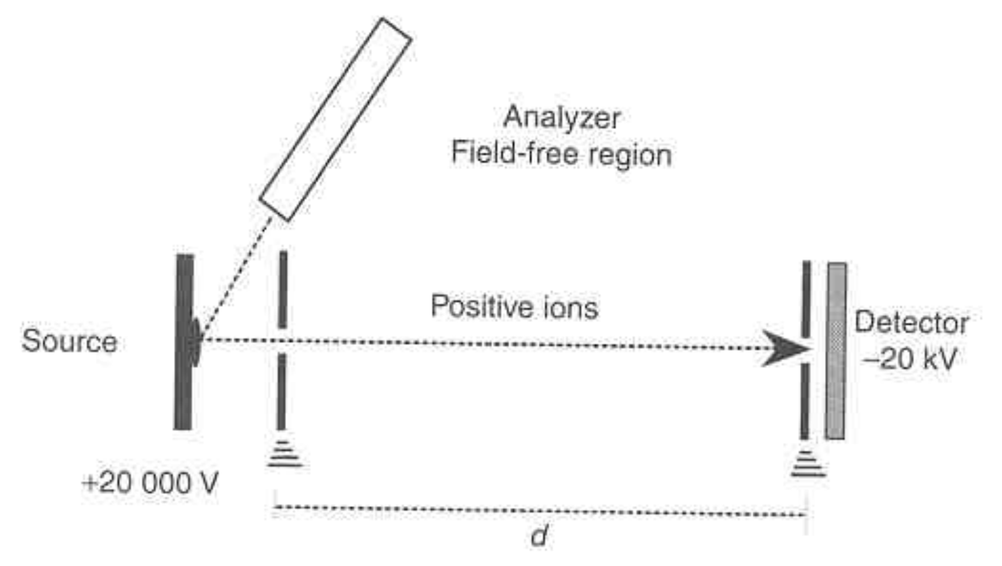


Speed ∝ distance ∝ time

Speed ∝ mass ∝ Kinetic Energy

Did you ever take logic classes?

TIME OF FLIGHT : Equations of motion



In a linear TOF, neutral and charged fragments generated through fragmentation of ions in the drift region cannot be distinguished from the original ion, because their velocity remains the same.

$$\frac{mv^2}{2} = E_k = qV_s = zeV_s$$

For z=1

$$\boxed{v^2 = \frac{2eV_s}{m}}$$

$$v = \frac{d}{t} \longrightarrow \boxed{v^2 = \frac{d^2}{t^2}}$$

$$t = d\sqrt{\frac{m}{e2V_s}}$$

$$\boxed{\frac{m}{e} = \frac{2V_s t^2}{d^2}}$$

Spread in E_k is your worst problem!

Mass Analyzers: Pulse it to increase resolution

FIELD FREE REGION

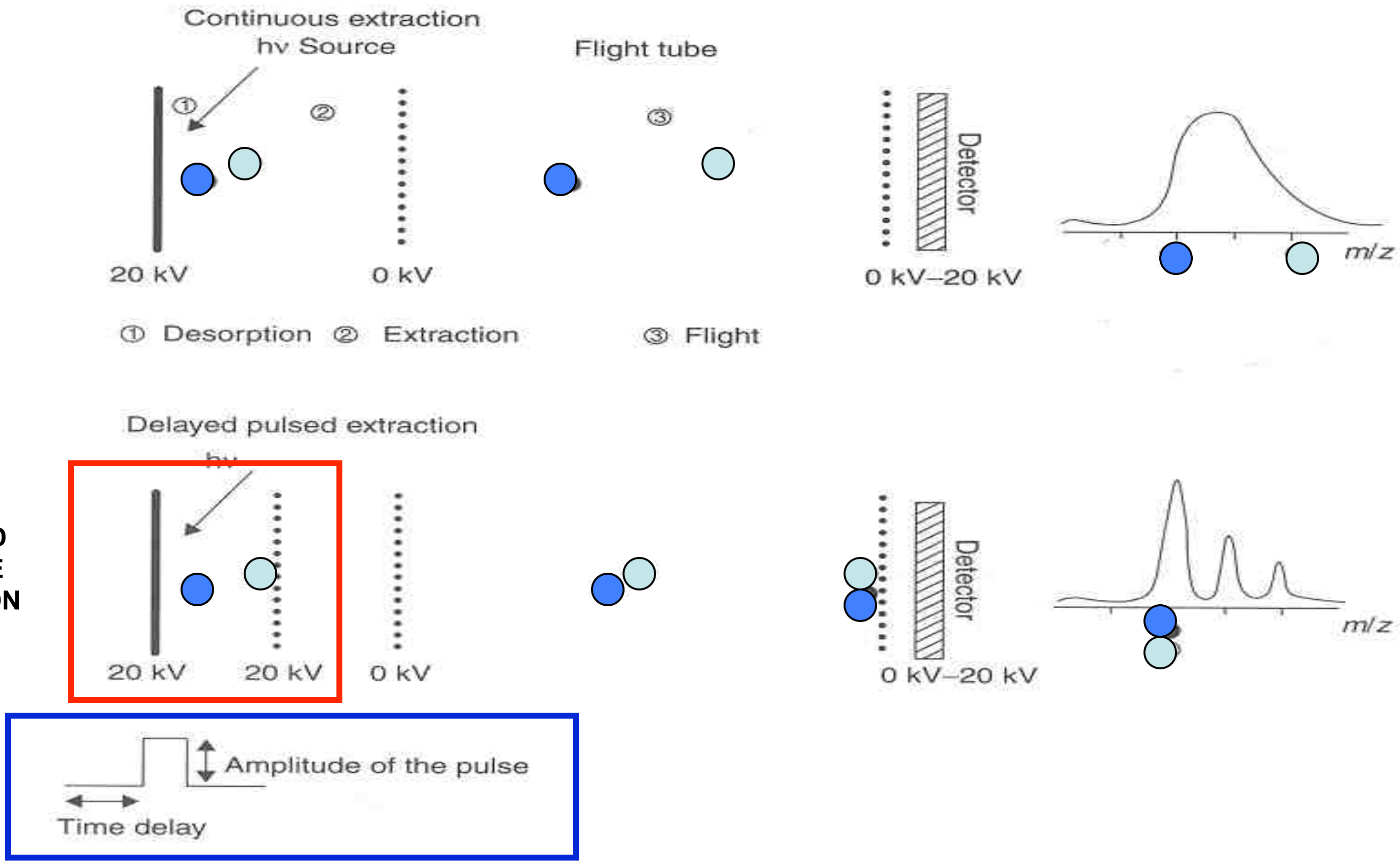
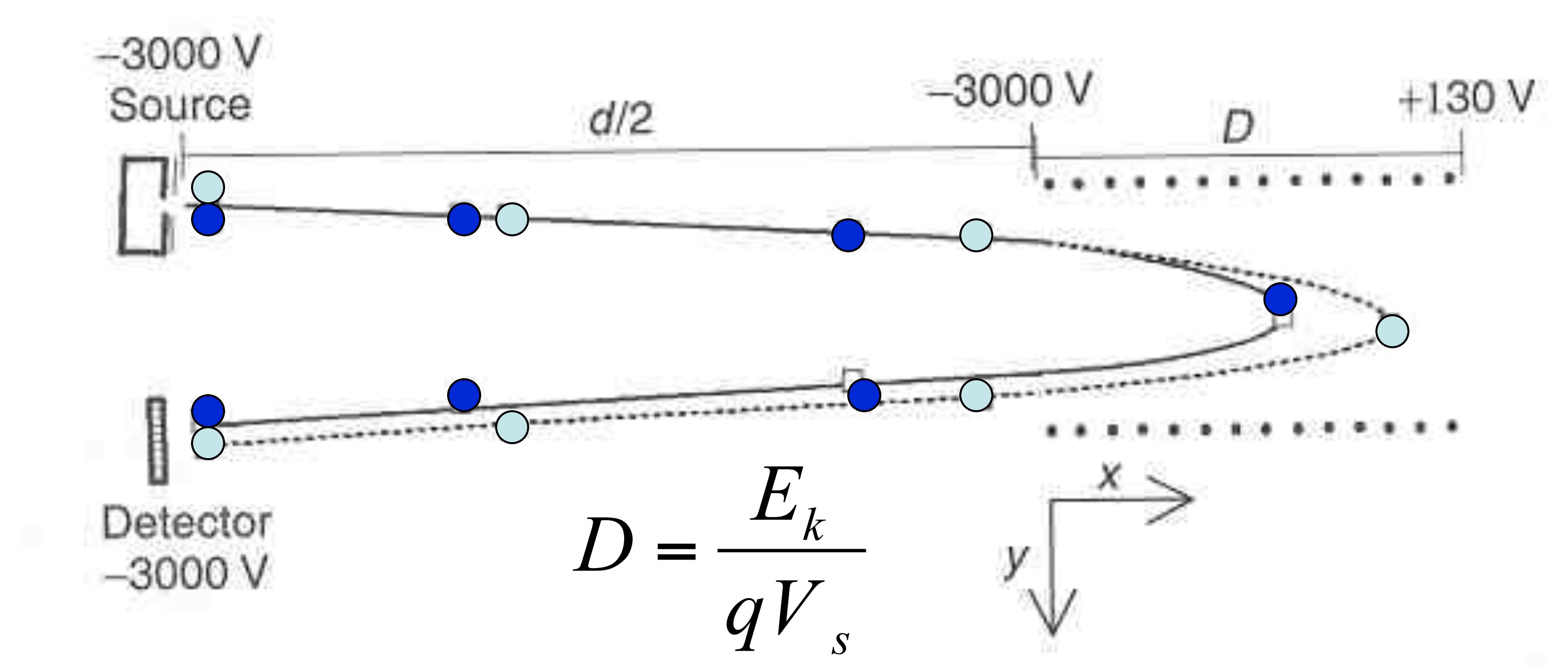


Figure 2.31
Schematic description of a continuous extraction mode and a delayed pulsed extraction mode in a linear TOF mass analyzer: (○) ions of a given mass with correct kinetic energy; (●) ions of the same mass but with a kinetic energy that is too low. Delayed pulsed extraction corrects the energy dispersion of the ions leaving the source with the same m/z ratio

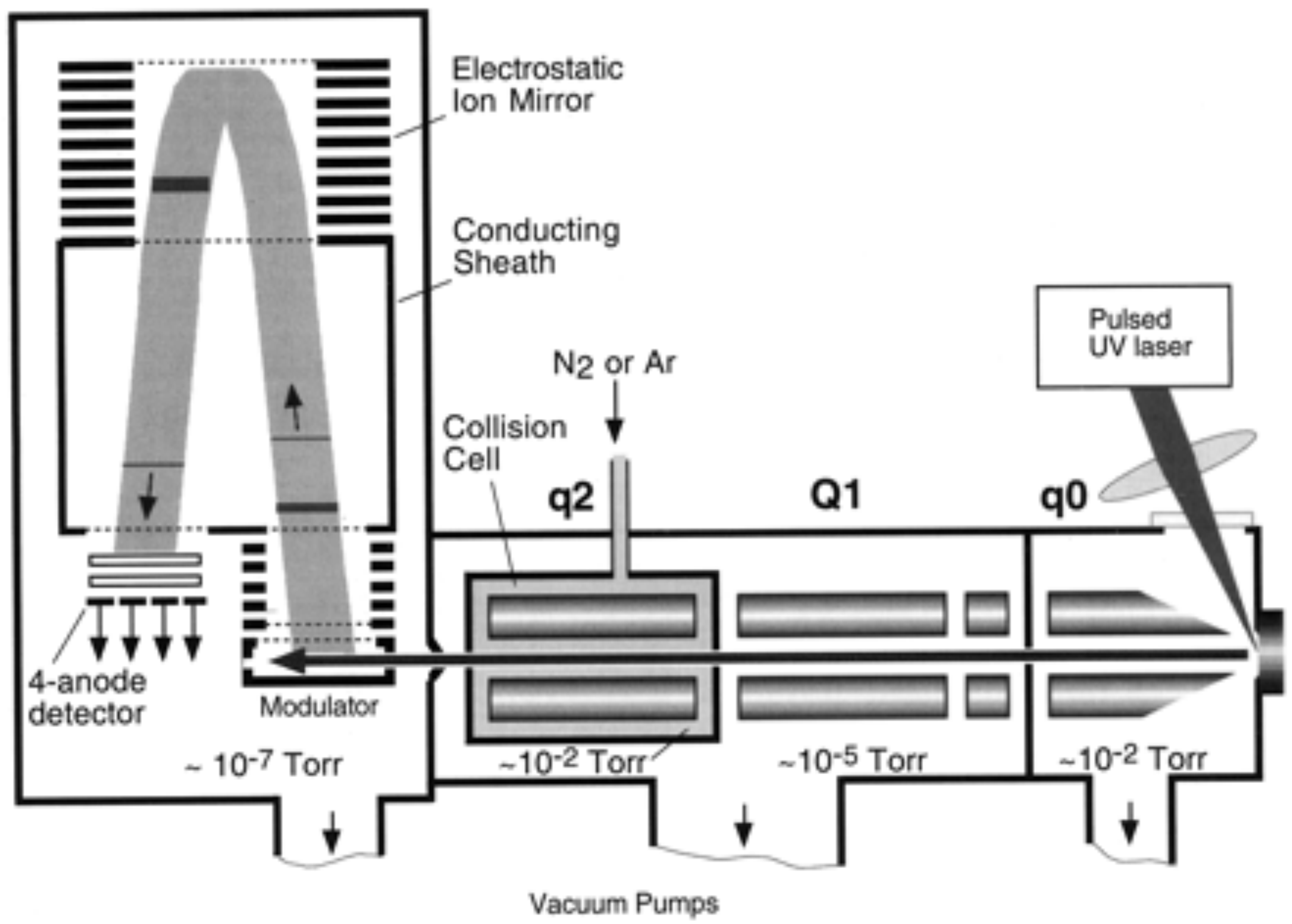
Mass Analyzers: TOF with REFLECTRON



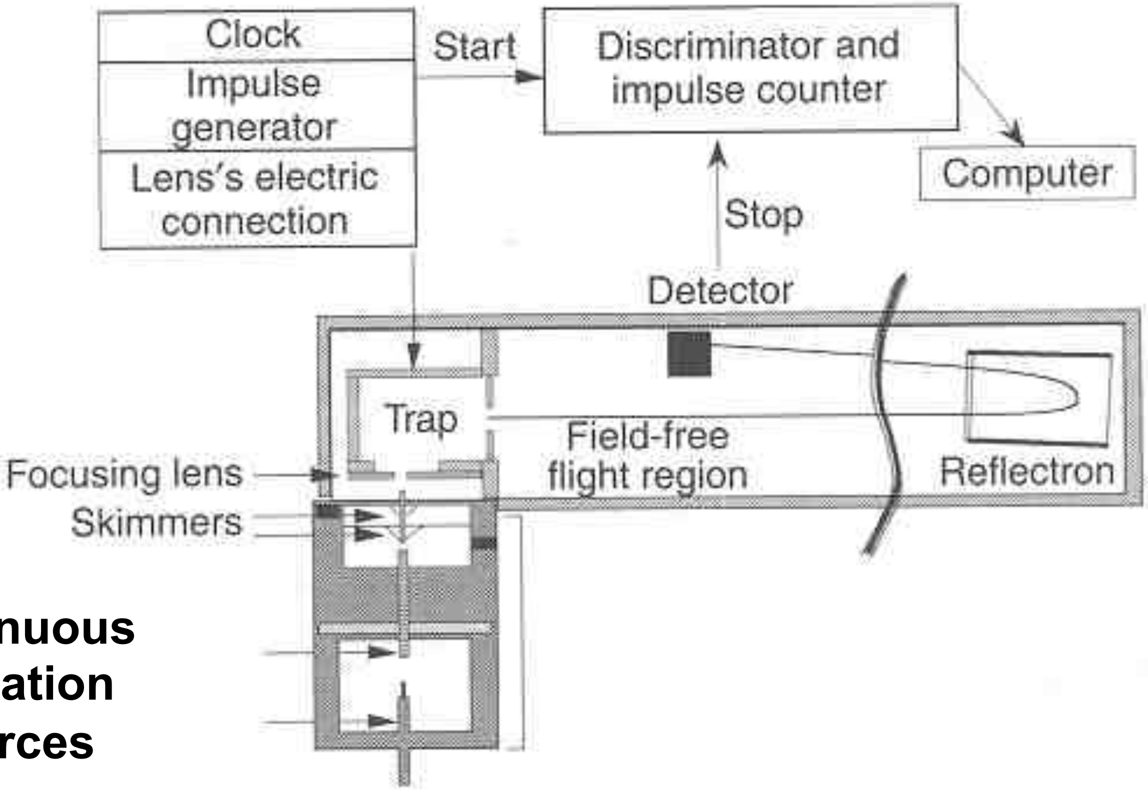
$$D = \frac{E_k}{qV_s}$$

Ion trajectories in a reflectron time-of-flight mass spectrometer, where E is the ion energy and δE the difference in ion energy of two ions

Mass Analyzers: TIME OF FLIGHT



TIME OF FLIGHT: Versatility?



Continuous ionization sources

Figure 2.38
Coupling of a continuous ion source, here an electrospray, with a TOF instrument using an ion trapping device. (Reproduced (modified) from Ref. 36 with permission)

Mass Analyzers: TIME OF FLIGHT

Benefits

- Fastest MS analyzer
- Well suited for pulsed ionization methods (method of choice for majority of MALDI mass spectrometer systems)
- High ion transmission
- MS/MS information from post-source decay
- Highest practical mass range of all MS analyzers

Limitations

- Requires pulsed ionization method or ion beam switching (duty cycle is a factor)
- Fast digitizers used in TOF can have limited dynamic range
- Limited precursor-ion selectivity for most MS/MS experiments

Applications

- Almost all MALDI systems
- Very fast GC/MS systems

Mass Analyzers: ICR-MS, the sound of ions

$$F = qvB$$ **Centripetal**

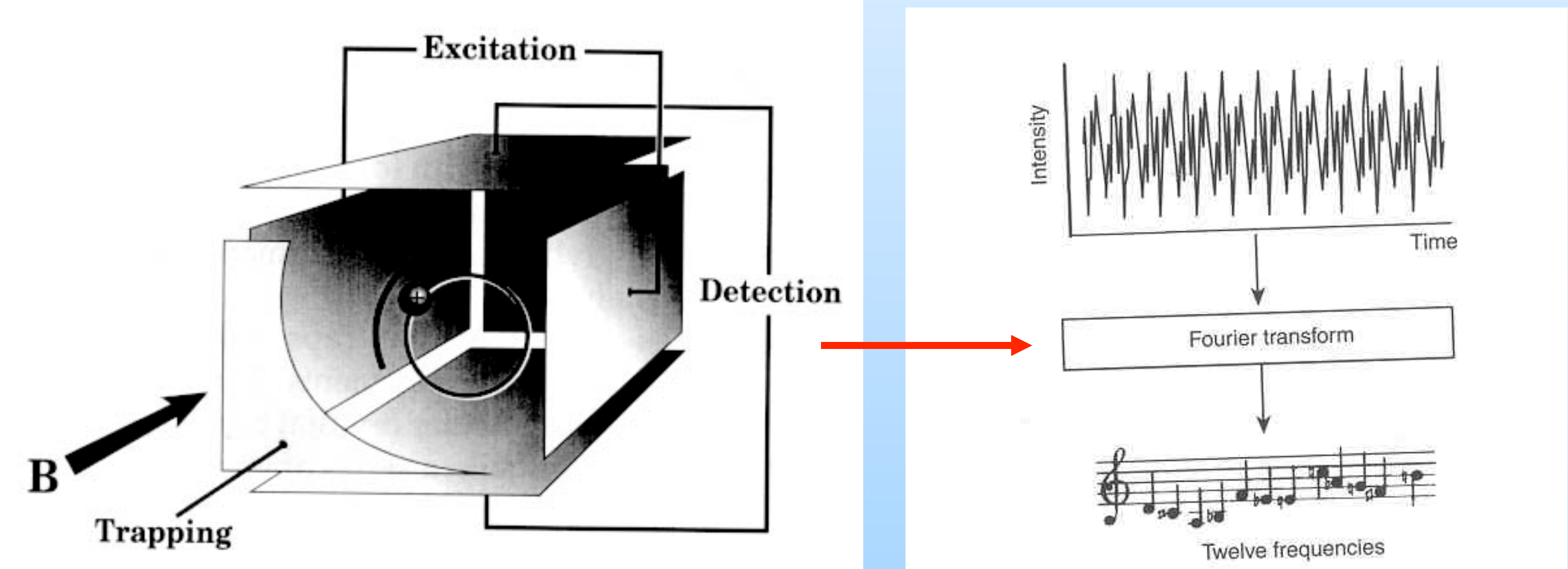
$$F' = \frac{mv^2}{r}$$ **Centrifugal**

$$qB = \frac{mv}{r}$$

$$\upsilon = \frac{v}{2\pi r}$$ **Frequency**

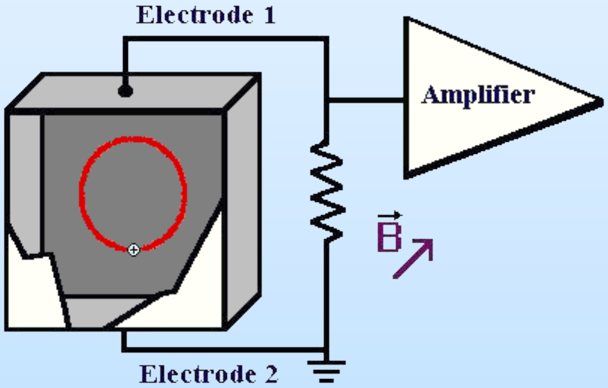
Angular velocity

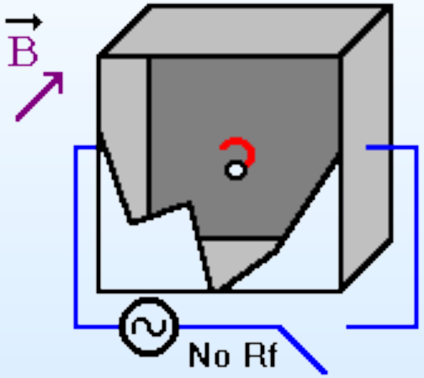
$$\boxed{\omega_c = 2\pi\upsilon = \frac{v}{r} = \frac{q}{m}B}$$



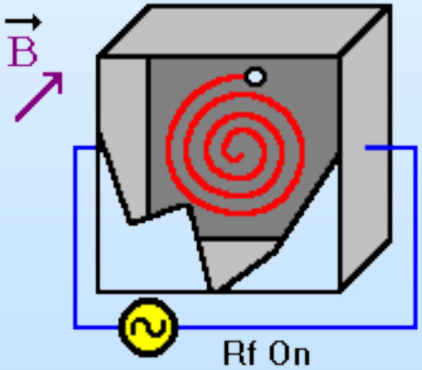
Mass Analyzers: ICR

$$\frac{mv^2}{r} = evB \qquad \omega = \frac{v}{r} = \frac{eB}{m}$$

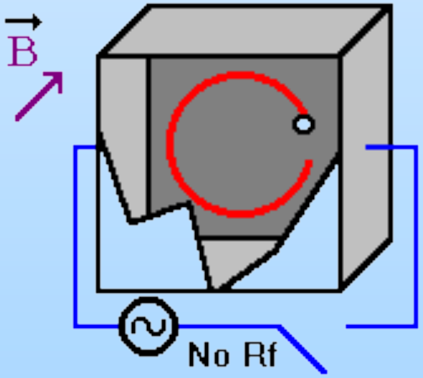




1) Ions before excitation. They are in their natural cyclotron radius within the magnetic field.

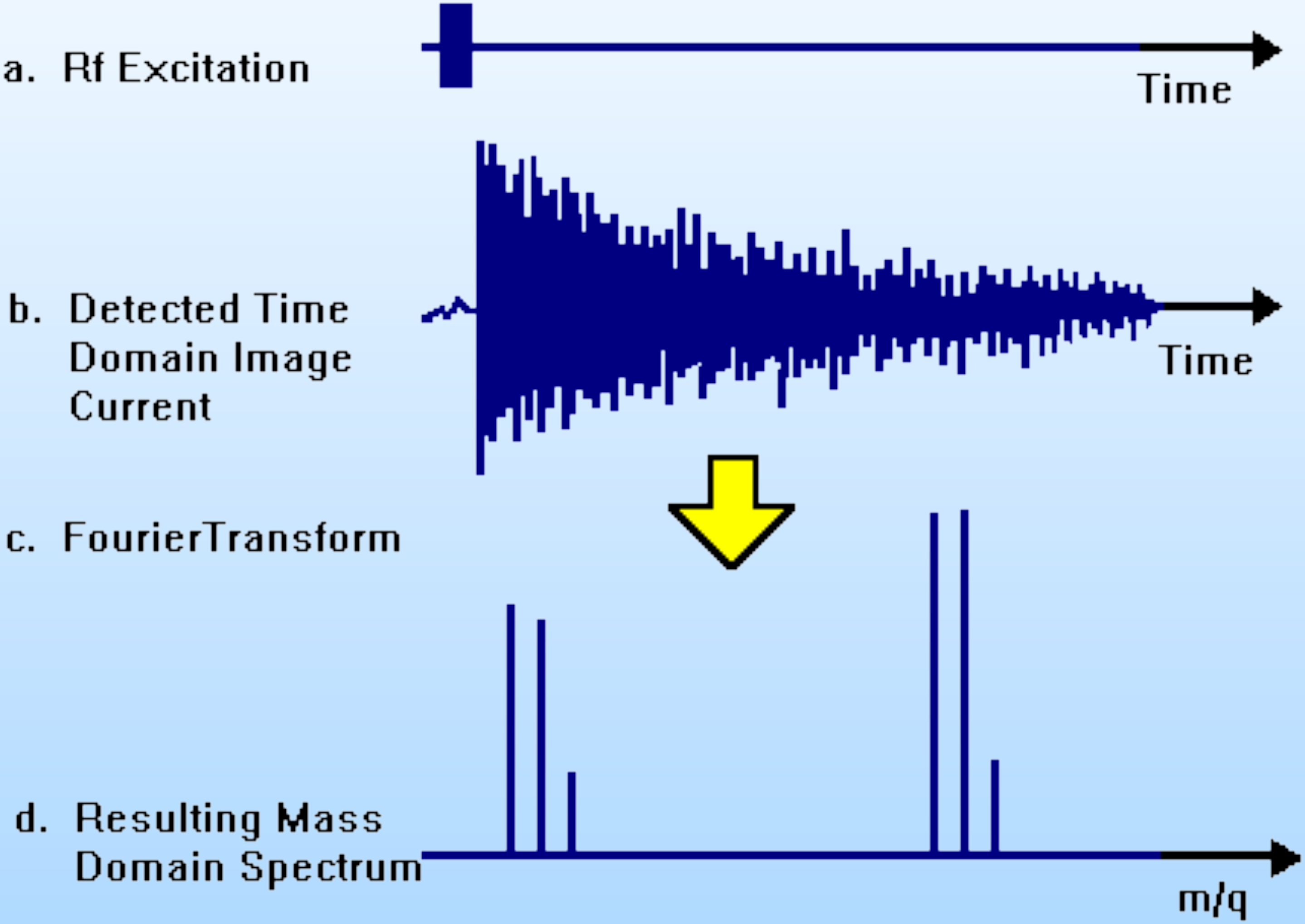


2) Ions during excitation with a radio frequency. This excites the ions to a larger cyclotron radius.



3) Ions after excitation. The cyclotron radius remains in its larger state.

Mass Analyzers: ICR



Mass Analyzers: ICR

Benefits

- The highest recorded mass resolution of all mass spectrometers
- Powerful capabilities for ion chemistry and MS/MS experiments
- Well-suited for use with pulsed ionization methods such as MALDI
- Non-destructive ion detection; ion re-measurement
- Stable mass calibration in superconducting magnet FTICR systems

Limitations

- Limited dynamic range
- Strict low-pressure requirements mandate an external source for most analytical applications
- Subject to space charge effects and ion molecule reactions
- Artifacts such as harmonics and sidebands are present in the mass spectra
- Many parameters (excitation, trapping, detection conditions) comprise the experiment sequence that defines the quality of the mass spectrum
- Generally low-energy CID, spectrum depends on collision energy, collision gas, and other parameters

Applications

- Ion chemistry
- High-resolution MALDI and electrospray experiments for high-mass analytes
- Laser desorption for materials and surface characterization